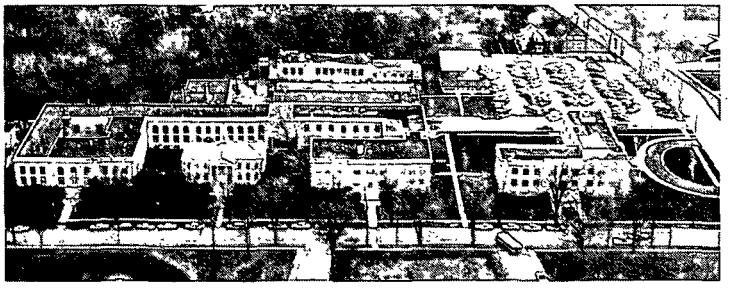

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RAMAN SPECTROSCOPIC STUDIES OF LIGNIN IN NATIVE WOODY TISSUE

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Raman Spectroscopic Studies of Lignin in Native Woody Tissue

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RAMAN SPECTROSCOPIC STUDIES OF LIGNIN IN NATIVE WOODY TISSUE

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ABSTRACT

In previous reports we have described the use of Raman spectroscopy in studies of celluloses and chemical pulps. We are now extending the use of this technique to investigations of lignins. In the present report we describe experiments carried out to assess the feasibility of detecting the Raman spectra of native lignins. The approach is based on recording the spectra of groundwood, subjecting it to successive delignification treatments, and subtraction of the spectra of the final pulp to identify the spectral features associated with residual lignin at each stage.

BACKGROUND

We have discussed in detail elsewhere the advantages of using Raman spectroscopy in the study of pulp and woody tissue (1). The key factors are: 1. The possibility of recording spectra with little interference from moisture; 2. The clear possibility of separating effects due to Rayleigh scattering; 3. The high dependence on vibrational motions of covalent bond systems, making the spectra particularly sensitive to molecular architecture and conformational variation; 4. The greater convenience of working with frequencies in the visible and near infrared domains of the electromagnetic spectrum.

Experimentally, the acquisition of Raman spectra requires exposure of the sample under investigation to an intense source of exciting radiation, and examination of the spectral distribution of the scattered radiation. The intensity of light at frequencies shifted relative to the exciting radiation provides a measure of the exchange of vibrational spectral energy between the sample and the exciting electromagnetic field. The information content is not unlike that of an infrared spectrum, except that the intensity associated with a particular vibrational mode is highest for the least polar motions; in this respect Raman spectra are complementary to infrared spectra.

Although detailed interpretation of the spectra of lignins is not possible without rather complex normal coordinate analyses, some spectral features can be informative when they are examined in conjunction with normal coordinate analyses of model compounds. Recent completion of such an investigation of lignin model compounds at our Institute (2) provides the background against which results of our present preliminary study are interpreted.

EXPERIMENTAL

The starting material consisted of air dried chips from loblolly pine (Pinus taeda L.). They were ground in a Wiley mill to pass through 40-mesh screen. The resulting wood meal was subjected to vacuum-assisted extraction in the following sequence: ethanol; chloroform:ethanol (2:1); ethanol; ethanol:water (1:1); water. It was then delignified by treatment with acid-chlorite at 70 deg. C (160 mL distilled water; 0.5 mL glacial acetic acid; 1.5 g $NaClO_2$ per 5 g air-dried wood meal). A small portion of wood meal (approximately 0.2 g) was removed after each hour of treatment, at which time pulping chemicals were replinished. The samples were extensively washed with distilled, deionized water immediately after removal.

The original groundwood and those treated for different periods of time were subjected to the following measurements: 1. Raman spectra; 2. FTIR diffuse reflectance spectra; 3. Klason lignin; 4. Acid soluble lignin. The Raman spectra were acquired using 514.5 nm excitation; all are the result of multiple scans. The infrared diffuse reflectance spectra were acquired with a Nicolet model 7199 spectrometer. Subtractions and integrations were carried out using the software of the dedicated computers for the respective instruments.

RESULTS AND DISCUSSION

The Raman spectra are shown in Figure 1. The spectrum of the untreated wood is clearly dominated by the 1595 cm^{-1} ring stretching mode of the aromatic rings in lignin, while that of the sample treated for 6 hours is typical of the celluloses from wood pulps, except for the small residue of the lignin peak at 1595 cm^{-1}. The spectra of intermediate samples show the changes resulting from the progressive removal of the lignin.

The changes in the spectra are highlighted more clearly in Figure 2, which represents the results of subtraction of the spectrum of the sample treated for 6 hours from all of the preceeding spectra. Clearly the most dramatic change occurs during the first hour of treatment.

This is shown in Figure 3, where the intensity of the 1595 cm^{-1} band is plotted against lignin content. The intensity of the band in the original wood is a little over 4 times that of its intensity after the first period of treatment.

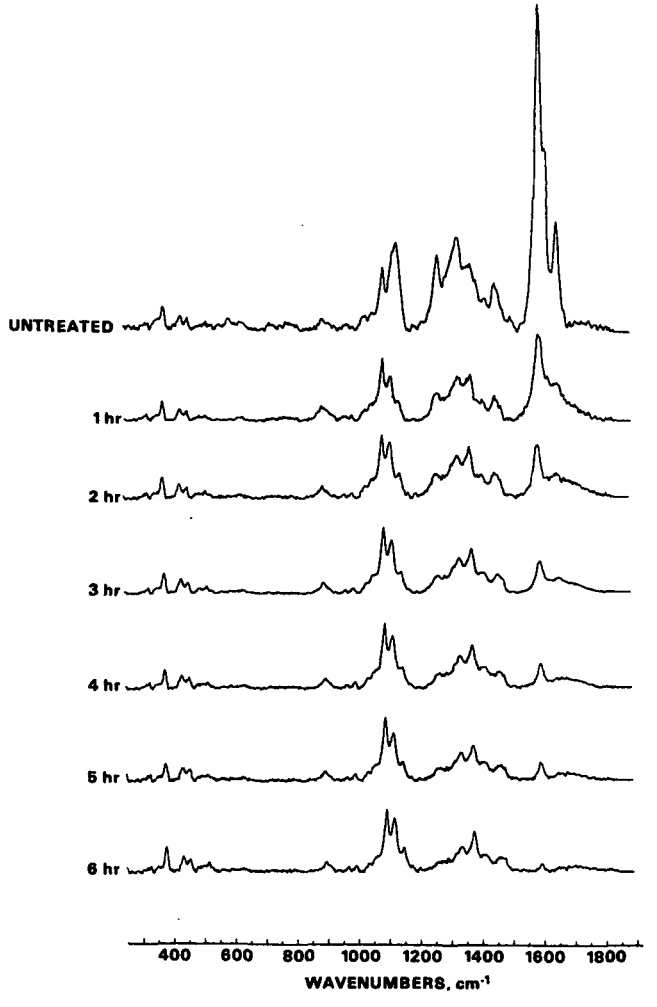

Figure 1. Raman spectra of wood meal from loblolly pine before and after delignification for 1 to 6 hours.

Another interesting feature which is obvious in Figure 2, is the total disappearance of the 1138 cm^{-1} band during this same interval. The other bands in the spectra appear to decay in proportion to the residue of the 1595 cm^{-1} band.

Finally, it is clear that the contribution of lignin to the low frequency portion of the spectrum is very limited indeed. This is consistent with the pattern observed by Ehrhardt (2) for the lignin model compounds, where, with regularity, the spectra were dominated by one or another of the symmetric stretching vibrations of the aromatic rings.

A discussion of all the features in the spectra are beyond the scope of this report, but two observations are worthy of note. The first is the rapid decline of the 1595 cm^{-1} band during the first interval, and the correlated decline of the 1138 cm^{-1} band. These suggest a common origin in aromatic rings with a distinctive pattern of substitution, which may be particularly sensitive to attack under the conditions of delignification. The studies on model compounds suggest that the 1138 cm^{-1} band has its origin in the stretching vibration between the aromatic ring and one of its substituent groups. If this is indeed the case, this substituent group must be one that has an effect on the scattering coefficient of the 1595 cm^{-1} band. We are actively assessing the validity of this interpretation.

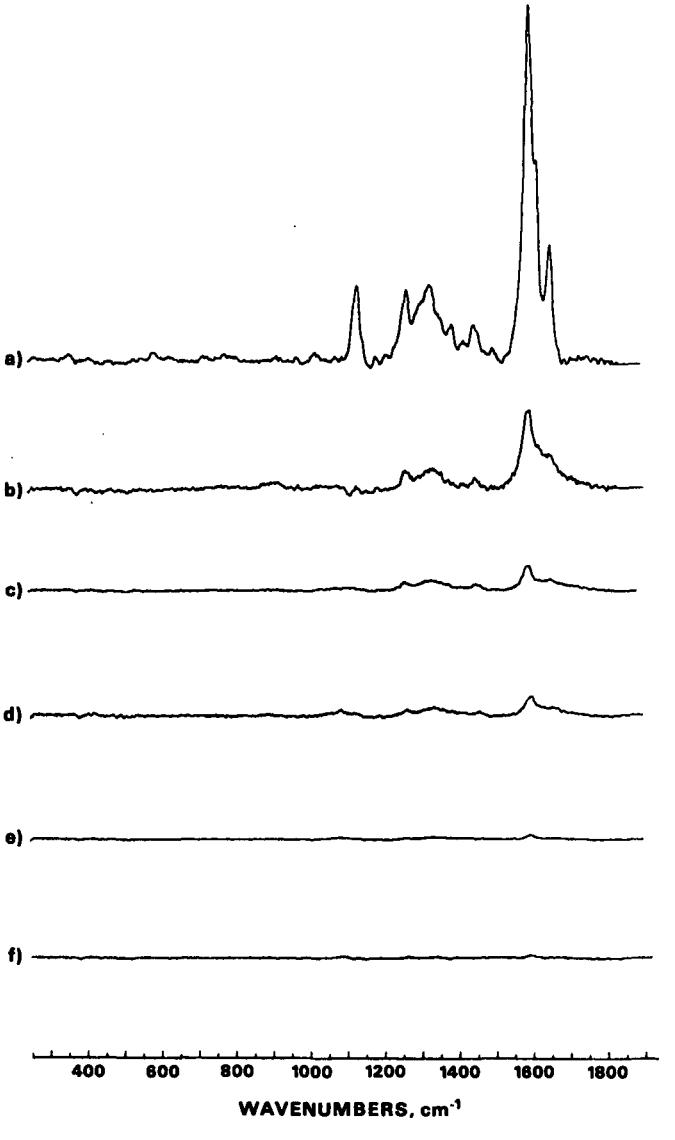

Figure 2. Difference spectra comparing the first six samples with the sample treated for six hours.

The second interesting feature is the linearity of the plot in Figure 3, apart from the value for the original wood sample. The quality of this fit is superior to those derived from the

1510 and the 1590 cm^{-1} bands in the FTIR diffuse reflectance spectra. Though this observation needs to be investigated further, it may reflect a lower sensitivity of the intensity of the aromatic ring stretching bands to substituents in the Raman effect than in infrared absorption. Thus, as the distribution of substituents on the aromatic rings varies during the progress of delignification, the absorption coefficients of the infrared bands will change over a wider range than the scattering coefficients of the Raman bands.

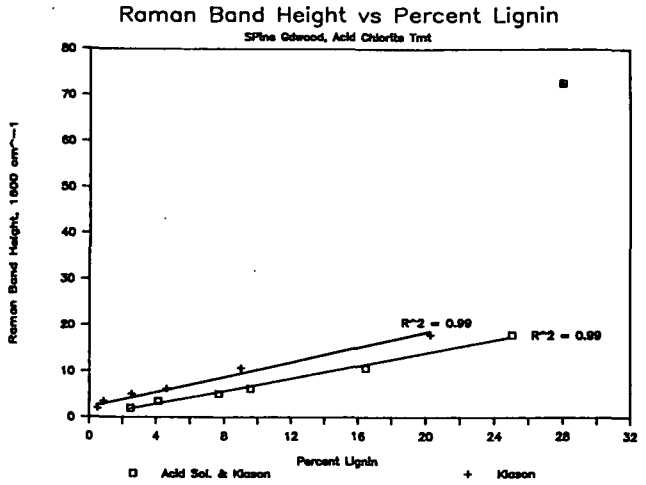

Figure 3. Variation of the intensity of the 1595 cm^{-1} band with lignin content.

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2. EHRHARDT, S. M. Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, Wisconsin 1984.